United States Patent Application for

SYNTHESIS OF TETRAGONAL PHASE STABILIZED NANO AND SUBMICRON SIZED NANOPARTICLES
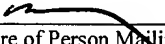
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SYNTHESIS OF TETRAGONAL PHASE STABILIZED NANO AND SUBMICRON SIZED NANOPARTICLES

FIELD OF INVENTION

This invention relates to nanoparticles and more particular to monodispersed,

10   spherical ZrO_2 particles in the size range of approximately 10 to approximately 600 nm.

exhibiting metastable tetragonal crystal structure at room temperature and this invention

provides the synthesis, for the first time, using the sol-gel technique and without doping

any trivalent impurities, of monodispersed, spherical ZrO_2 particles in the size range of

approximately 10 to approximately 600 nm, exhibiting metastable tetragonal crystal

15   structure at room temperature. This invention has revealed using high-resolution

transmission electron microscopy that "hard-aggregates" forming tendency of ZrO_2

nanocrystallites of size approximately 30 to approximately 45 nm is responsible for

stabilizing the high-temperature metastable tetragonal phase, at room temperature within

large sized (500-600) undoped ZrO_2 particles.

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BACKGROUND AND PRIOR ART

Zirconium (ZrO_2) is a well-known structural ceramic, which exhibits tetragonal-

to-monoclinic martensitic phase transformation. This phase transformation is of

technological importance as it contributes to the toughening of ceramics. Porter, D.L.,

Evans, A.G., Heuer, A. H., Acta Metall, 1979, 27, 1649. The tetragonal-to-monoclinic

phase transformation is accompanied by volume expansion and can be triggered by

hydrostatic and shear stresses. See Simha, N., Truskinovsky, L. Acta Metall. Mater.

1994, 42, 3827.

5   This type of transformation can take place near the crack tip due to local stress

concentration, which can blunt the crack tip as a result of the development of

compressive stresses associated with the phase transformation; thus, delaying the crack

propagation and resisting subsequent fracture.

Zirconia is used as a dispersed phase in oxide (alumina) (Kosmac, T, Swain,

10   M.V. Clausssen, N, Mater. Sci Eng. 1984, 71,57). as well as non-oxide (carbides,

borides, and nitrides) (Swain, M.V. Mater. Forum 1988, 11, 182.) ceramics to increase

their fracture toughness, strength, and hardness. This stress induced transformation has

also been shown to increase the plasticity from the shape deformation and

accommodation strains, which are associated with the transformation. (Muddle, B. C.

15   Kelly, P.M. MaterForum 1988, 11, 182.) Increase in the wear and corrosion resistance of

nanostructured ceramic coatings as a result of stress-induced phase transformation has

also been reported. (Aita, C.R., In Advances in Catings: TMS Annual Meeting,

Warrendale, PA, 1995 p. 235) Besides this, tetragonal ZrO_2 also finds application as

catalyst/catalyst support for various gas-phase reactions. (Haruta, M. Kobayashi, T, Sano,

20   H., Yamada, N Chem Lett. 1987, 829, 405 and Knell, A, Barnickel, P, Baiker, A,

Wokaum, A. J. Catal. 1992, 137, 306.) Hence, synthesizing ZrO2 particles with

metastable tetragonal crystal structure is important.

Doping zirconia with trivalent impurities has been a traditional approach for the

metastable tetragonal phase stabilization. (Ping, L, Chen, L.W., Penner-Hahn, J.E., J.Am

Ceram Soc. 1994, 77, 188.)   Particle size has also been observed to have its own effect

on the metastable tetragonal phase stability in nanocrystalline zirconia. (Garvie, R. C., J.

5   Phys. Chem 1965, 69, 1238, and Nitsche, R, Rodewald, M, Skandan, G, Guess, H., Hahn,

H. Nanostruct. Mater. 1996, 7, 535, and Nitsche, R, Winterer, M, Hahn, H, Nanostruct.

Mater. 1995, 6, 1979). Due to the existence of a critical nanoparticle size for the

metastable tetragonal phase stabilization, the tetragonal phase stabilization within the

submicron sized ZrO_2 particles has been unachievable.

10   <u>SUMMARY OF THE INVENTION</u>

The first objective of this invention is to provide ultra fine approximately 10 to

approximately 600 nm and more particularly approximately 10 to approximately 30 nm

and sub-micron sized (approximately 500 to approximately 600 nm) ZrO_2 nanoparticles

that are in the metastable tetragonal phase.

15   The second objective of this invention is to provide a method for synthesizing

particles of the size range of approximately 10 to approximately 600 nm and more

particularly nano (approximately 10 to approximately 30 nm) and sub micron

(approximately 500 to approximately 600 nm) ZrO_2 nanoparticles in the metastable

tetragonal phase.

20   The third objective is to provide coatings of ZrO_2 coatings on metal substrates.

A preferred embodiment of the invention includes monodispersed, spherical

zirconia (ZrO_2) particles of approximately 10 to approximately 600 nm, which exhibit

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metastable tetragonal crystal structure at room temperature. The ZrO_2 particles are

approximately 100% in the tetragonal phase at room temperature, and the particles are

pure and free of foreign oxides.

A preferred method for the synthesis of monodispersed, spherical ZrO_2 particles,

5   which exhibit approximately 100% metastable tetragonal structure at room temperature,

of sizes of approximately 10 to approximately 600 nm, in powder form can include

various steps. The initial step can include mixing zirconium-alkoxide and an alcohol,

forming preparation one, followed by separately dissolving completely de-ionized water

and a polymeric steric stabilizer in an alcohol forming preparation two. Next the

10   preparation one and the preparation two can be mixed with vigorous stirring for a

approximately few minutes only, subjecting the materials to hydrolysis and condensation

reactions with very slow stirring. Next, there is waiting for the formation of a sol from

the mixture. Next, there is drying at approximately 80 degrees C to form resultant

material followed by crushing the resultant material.

15   The polymeric steric stabilizer can be an organic polymer containing -OH or

ether group. The polymeric steric stabilizer can be from one of the group consisting of

hydroxypropyl cellulose polymer (HPC), polyvinylalcohol, ethylene glycol, and

hexamethyldisilazane. The zirconium-alkoxide can be zirconium (IV) n propoxide and

the alcohol can be anhydrous alcohol. Synthesis can take place under normal

20   atmospheric conditions. The polymeric steric stabilizer can be an HPC polymer, and

have a molecular weight of approximately 80,000 to approximately 1,000,000.

Further objects and advantages of this invention will be apparent from the following detailed description of the presently preferred embodiments which are illustrated schematically in the accompanying drawings.

<u>BRIEF DESCRIPTION OF THE FIGURES</u>

5   Fig. 1a shows nanocrystalline (approximately 20 to approximately 25 nm) sized spherical ZrO_2 particles synthesized using the sol-gel technique under the processing conditions of $R = 60$ and HPC = 1.0 g/L.

Fig. 1b shows monodispersed, submicron sized approximately 500 to approximately 600 nm spherical ZrO_2 particles synthesized using the sol-gel technique under

10   processing conditions of $R = 5$, and HPC= 1.0 g/L.

Fig. 2a shows HRTEM analysis of monodispersed submicron sized spherical ZrO_2 particles synthesized under the processing conditions of R=5 and HPC =1.0 g/L after calcinations at 400 degrees for 2 hours.

Fig. 2b shows the SAED patterns obtained for monodispersed, submicron sized

15   (approximately 500- approximately 600 nm) spherical ZrO_2 particles at the edge of a particle after calcination at 400 degrees C for 2 hours.

Fig. 2c shows SAED patterns obtained for monodispersed submicron sized (approximately 500 to approximately 600nm) spherical ZrO_2 particles at the center of a particle after calcinations at 400 degrees C for 2 hours.

20   Fig. 3 shows typical broad scan XRD patterns, within 2θ range of 10 degrees to 80 degrees, obtained for nanocrystalline ZrO_2 particles of size approximately 20 to approximately 25 nm after calcinations at 400 degrees C for 2 hours, synthesized under the processing conditions of R =60, and HPC = 1.0 g/L.

Fig. 4 shows typical broad scan XRD patterns, within 2ι range of approximately 10° to approximately 80°, obtained for monodispersed, submicron sized (approximately 500 to approximately 600 nm), spherical ZrO_2 particles, after calcination at 400°C for 2 h, synthesized under the processing conditions of $R = 5$, and HPC=1.0 g/L.

5   Fig. 5 shows typical narrow scan XRD patterns obtained for monodispersed, submicron sized (approximately 500 to approximately 600 nm), spherical ZrO_2 particles, after calcination at higher temperatures for 2 h, synthesized under the processing conditions of $R = 5$, and HPC=1.0 g/L.

Fig. 6a provides schematic diagrams showing the ZrO_2 nanocrystallites forming loose-

10   aggregates.

Fig 6b provides schematic diagram showing the ZrO_2 nanocrystallites forming hard-aggregates.

Fig 6c provides a schematic representation of the athermal nature of tetragonal to monoclinic phase transformation in nanocrystalline ZrO_2. The calcination temperature

15   increases from (i) to (iii) represents the temperature range of 400-800°C.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Before explaining the disclosed embodiments of the present invention in detail it is to be understood that the invention is not limited in its application to the details of the particular arrangements shown since the invention is capable of other embodiments.

20   Also, the terminology used herein is for the purpose of description and not of limitation.

This invention demonstrates for the first time that, at room temperature, the stability of the metastable tetragonal phase within the submicron sized ZrO_2 particles

strongly depends on the aggregation tendency of ZrO_2 nanocrystallites. As a result of

strong aggregation of ZrO_2 nanocrystallites, the inventors have been able to synthesize

both nano (approximately 10 to approximately 30 nm) and large sized (approximately

500 to approximately 600 nm) ZrO_2 particles having 100% tetragonal crystal structure.

5   This particle size is much larger than the critical size of approximately 6 nm, reported in

the prior art, for the stabilization of 100% tetragonal phase.

To prepare the nanoparticles of the invention, pure zirconium(IV) n-propoxide

anhydrous ethanol (approximately 200 proof) and the HPC polymer

(hydroxyproylcellulose, molecular weight approximately 80,000 g/mol) used as a

10   polymeric steric stabilizer were obtained from Aldrich Co and were used as received

Other alcohols and zirconium alkoxides may also be used. Other polymeric

steric stablilzers may also be used such as any compound with -OH or ether groups, for

example polyvinylalcohol, ethylene glycol, or hexamethyldisilazane .

Other ceramic oxides can be used in addition to zirconium, for example, tin,

15   indium, and titanium.

Nanocrystalline ZrO_2 powder is synthesized by hydrolysis of zirconium (IV) n-

propoxide in an alcohol solution. The beakers used in the experiments were cleaned,

washed with deionizer water, dried completely and rinsed with anhydrous 200 proof

ethanol. During synthesis, two different but equal parts of alcohol solutions were

20   prepared. In the first part, deionized water was dissolved into anhydrous 200 proof

ethanol using two different R values (R)=5 and 60, which is the ratio of molar

concentration of water to zirconium(IV) n-propoxide. HPC polymer (HPC) =1.0 g/L was

then added to this part and was dissolved completely by stirring the solution overnight

using a magnetic stirrer. The second part of the alcohol solution was then prepared by

completely dissolving zirconium (IV) *n*-propoxide (0.1 M) in anhydrous 200 proof

ethanol under normal atmospheric conditions and homogenized using magnetic stirring

for a few minutes only. After preparing each solution, both the beakers were sealed

5   immediately with paraffin tape. Hydrolysis of zirconium(IV) *n*-propoxide was then

carried out under atmospheric conditions by rapidly mixing the two sealed solutions

under vigorous stirring. The formation of ZrO2 particles was evident from the white

color of the resulting sol due to immediate precipitation.

The sol was stirred very slowly for approximately 4 hours and then held under

10   static conditions for 24 h to ensure completion of the hydrolysis and condensation

reactions. The sol was subsequently dried at approximately 80°C using Petri dishes in

order to remove the solvent completely. The small gel pieces obtained were then crushed

to obtain the nanocrystalline ZrO_2 powder, which was calcined at different temperatures

ranging from approximately 400° to approximately 800°C in air for the phase evolution

15   study. The samples were heated at a rate of approximately 30°C/min up to the

calcination temperature, held at that temperature for 2 hours, and then slowly cooled to

room temperature in the furnace. The as-synthesized nanocrystalline ZrO2 powders were

then examined using a Phillips EM400 transmission electron microscope (TEM) at 120

kV. A high-resolution field TEM (HRTEM) (FEI-Philips Tecnai F30) was used to

20   observe lattice images showing different orientations of nanocrystals within a submicron

sized ZrO_2 particle, after calcination at approximately 400°C for 2 h.. Bright field TEM

images at 300 kV were taken to observe the lattice. Selected-area electron diffraction

(SAED) patterns were taken to analyze the crystal structure. SAED patterns collected

near the edge and from the center of the particle, provided the presence of nanocrystals within a submicron sized particle.

The crystalline phases present in the as-synthesized and calcined powders were also determined using a standard Rigaku X-ray diffractometer (XRD). Line traces were

5   obtained over 2ι values ranging from approximately 10° to approximately 80°. Narrow scan analysis was conducted in the 2ι range of approximately 29.5° to approximately 31.5°, as it contained the strongest line for the tetragonal $(111)t$ phase. This intense peak was then curve fitted using the peak-fit software (peak-fit, version-4, SPSS Inc.). The average tetragonal crystallite size (Dt) was calculated from the $(111)t$ diffraction peak

10   using Scherrer's equation, where, D is the average crystallite size in nm, $\ddot{I}$ is the radiation wavelength (approximately 0.154 nm), ß' is the corrected halfwidth at half-intensity (fwhm) and ι is the diffraction peak angle.

TEM images of nanocrystalline and submicron sized ZrO_2 particles synthesized via the sol-gel technique, under the processing conditions of R) 60 and R) 5, at

15   [HPC])g/L, are shown in Figures 1a and 1b, respectively. ZrO_2 nanocrystallites of size approximately 20 to approximately 25 nm are synthesized under the processing conditions of R) 60, [HPC]) approximately 1.0 g/L, Figure 1a. ZrO_2 nanocrystallites form "loose-agglomerates" under these processing conditions. On the other hand, monodispersed, submicron sized (approximately 500 to approximately 600 nm), spherical

20   ZrO_2 particles are formed under the synthesis conditions of R) 5, [HPC]) 1.0 g/L, Figure 1b. An HRTEM image obtained from the edge of one of the ZrO_2 particle, Figure 1b, after annealing at 400°C for 2 h, is shown in Figure 2a.

Two tetragonal lattices are observed in Figure 2a having different relative orientations. SAED images obtained form the edge and the center of ZrO2 particle, Figure 1b, after annealing at approximately 400 °C for 2 h, are shown in Figures 2b and 2c, respectively. More diffraction spots are observed in the SAED pattern obtained from

5   the center of the ZrO_2 particle, Figure 2c, than are obtained from the edge of the particle, Figure 2b. In fact, we observed a gradual increase in the number of diffraction spots when traversed from the edge toward the center of the particle. This indicates that a larger number of nanocrystallites are located at the center of the particle than that at the particle edge. Typical broad-scan XRD patterns obtained for ZrO2 particles synthesized

10   under the two different processing conditions, Figure 1a, 1b are presented in Figures 3 and 4 respectively, as a function of calcination temperature. The as-synthesized ZrO2 particles are observed to be X-ray amorphous; however, they crystallize at the calcinations temperature of approximately 400 degrees C. ZrO_2 nanocrystallites of size approximately 20 to approximately 25 nm exhibit tetragonal and monoclinic crystal

15   structure after calcinations at approximately 400 degrees C for 2 h, as shown in Figure 3. Tetragonal-to-monoclinic phase transformation is observed at approximately 600 degrees C, which increases the relative volume fraction of monoclinic phase at the expense of the tetragonal phase. The phase transformation almost goes to completion after calcinations at approximately 800 degrees C.

20   Thus, gradual transformation of tetragonal phase to monoclinic phase is observed for ZrO_2 nanocrystallites of size approximately 20 to approximately 25 nm with increasing calcinations temperature within the range of approximately 400 to approximately 800 degrees C. On the other hand, monodispersed, submicron sized

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(approximately 500 to approximately 600 nm) spherical ZrO_2 particles do not exhibit

gradual phase transformation as a function of increasing calcination temperature, Figure

4. The high-temperature metastable tetragonal phase is observed to nucleate from the

amorphous phase at approximately 400°C and is also observed to be stable after

5   calcination at approximately 600°C. No monoclinic phase is detected at the calcination

temperatures of approximately 400°C and approximately 600°C. However, when

calcined at approximately 800°C, almost complete tetragonal to monoclinic phase

transformation is observed.

Typical narrow XRD scans of the (111)t peak, corresponding to the tetragonal

10   phase, for monodispersed, submicron sized, spherical ZrO_2 particles, after calcination at

approximately 400°C and approximately 600°C, are shown in Figures 5a and 5b,

respectively. The crystallite size of approximately 45 nm is calculated using Scherrer's

equation (Cullity, B.D., 1978. Elements of S-Ray Diffraction, Addison-Weley,

Massachusetts.) for monodispersed, submicron sized, spherical ZrO_2 particles after

15   calcination at approximately 400°C. Moreover, decrease in the FWHM is observed in

Figure 5 with increase in the calcination temperature.

TEM analysis reveals that the ZrO_2 nanoparticles of size approximately 20 to

approximately 25 nm synthesized at large R value 60 form "loose-agglomerates" as

schematically shown in Figure 6a. The formation of loose-agglomerates is due to high

20   nucleation rates associated with large R value. By contrast, XRD and HRTEM analysis

and corresponding SAED patterns obtained for monodispersed, submicron sized,

spherical ZrO_2 particles, after calcination at approximately 400°C, indicate that these

particles are made up of small nanocrystallites of size approximately 45 nm, as

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schematically shown in Figure 6b. It appears that ZrO_2 nanocrystallites form "hard-aggregates" under the processing conditions of R 5, [HPC]) 1.0 g/L, due to very slow kinetics of hydrolysis and condensation reactions associated with low R value.

The submicron sized ZrO_2 particles of size approximately 500 to approximately

5   600 nm are expected to exhibit monoclinic crystal structure at room temperature, as the particle size is much greater than the critical size of approximately 6 nm to have any thermodynamic effect for high-temperature metastable tetragonal phase stabilization. The tendency of the ZrO_2 nanocrystallites to form hard-aggregates and loose-agglomerates is, however, observed to significantly affect its phase transformation

10   behavior at higher temperatures.

The temperature of metastable tetragonal polymorph of ZrO_2 is stabilized at room temperature within the monodispersed submicron sized (approximately 500 to approximately 600 nm) spherical ZrO_2 particles without doping any trivalent impurity. Various theories have been proposed for the stabilization of metastable tetragonal phase

15   in nanocrystalline ZrO_2 at room temperature.

Garvie,(R.C. J Phy. chem, 1965, 69, 1238) experimentally (using XRD) and using thermodynamic calculations, showed the existence of a critical size of 20 nm, below which the metastable tetragonal phase is stable in nanocrystaline ZrO_2 and above which the monoclinic phase is stable. Mitsuhashi et al,,(J. Am. Ceram. Soc. 1974, 57,

20   97) however, showed that the metastable tetragonal phase can be stabilized in ZrO_2 nanocrystallites of size greater than approximately 30 nm due to the strain energy involved at the interphase boundaries resulting from the simultaneous presence of monoclinic and tetragonal phases within the crystallites. By HRTEM analysis Nitsche et

al further showed that the critical size for 100% tetragonal phase stabilization in nanocrystalline ZrO_2 is about 6 nm, above which ZrO_2 nanocrystallites exist as a core-shell particles with tetragonal phase, as a core and monoclinic phase as a shell. In our invention, ZrO2 nanocrystallites of size as small as about 20 to about 25 nm are

5 synthesized (Figure 1a) which are larger than the critical size of about 6 nm for the stabilization of the about 100% tetragonal phase. This is probably the reason for the appearance of tetragonal as well as monoclinic phases when these ZrO_2 nanocrystallites are calcined at the crystallization temperature of 400 degrees C. With increased calcinations temperature above 400 degrees C, the phase transformation possibly

10 proceeds in a manner as described schematically in Figure 6c.

The tetragonal-to-monoclinic phase transformation in ZrO_2 is athermal in nature. As a result, a specific amount of monoclinic phase is formed at each calcination temperature, as observed in Figure 3. As mentioned earlier, monodispersed, submicron sized (approximately 500 to approximately 600 nm), spherical ZrO_2 particles are

15 composed of small nanocrystallites of size approximately 45 nm after calcination at 400°C. The nanocrystallite size of approximately 45 nm is also larger than the predicted and observed critical size of approximately 30 nm[10] and approximately 6 nm[11,12] respectively for approximately 100% metastable tetragonal phase stabilization. However, interestingly, no monoclinic phase formation is observed after crystallization of

20 submicron sized ZrO_2 particles at 400°C, Figure 4.

Moreover, the nanocrystallites within the submicron sized ZrO2 particles are observed to grow due to calcination at 600°C, which is indicated by the decrease in the FWHM of the (111)t peak with increase in the calcination temperature. Even after the

growth of the nanocrystallites above approximately 45 nm size, no tetragonal to

monoclinic phase transformation is observed at approximately 600°C. Hence, the

tetragonal-to-monoclinic phase transformation appears to be suppressed within the

submicron sized ZrO_2 particles at 600°C. Thus, the phase evolution behavior exhibited

5   by the monodispersed, submicron sized (approximately 500 to approximately 600 nm),

spherical ZrO_2 particles is in contrast with that of ZrO_2 nanocrystallites of size

approximately 20 to approximately 25 nm.

It is noted that ZrO2 nanocrystallites (approximately 45 nm) form hard-aggregates

of size approximately 500 to approximately 600 nm, under the processing conditions of R

10   5, [HPC]) 1.0 g/L, while ZrO_2 nanocrystallites of size approximately 20 to

approximately 25 nm, synthesized under the processing conditions of R) 60, [HPC]) 1.0

g/L, form loose-agglomerates. It appears that due to the formation of hard-aggregates,

the tetragonal-to-monoclinic phase transformation, which is accompanied by volume

expansion, is suppressed at approximately 400°C and approximately 600°C. As a result,

15   monodispersed, submicron sized (approximately 500 to approximately 600 nm), spherical

ZrO_2 particles having metastable tetragonal crystal structure are successfully synthesized

in the present investigation.

The stabilization of metastable of tetragonal phase via proposed mechanism,

which involves the suppression of volume increase associated with the tetragonal-to-

20   monoclinic phase transformation, due to dense agglomeration of nanocrystallites within

monodispersed, submicron sized (approximately 500 to approximately 600 nm), spherical

ZrO_2 particles, is supported by the following observations. First, the volume expansion

associated with the tetragonal to monoclinic phase transformation would cause many

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stresses and strains to be included in the structure that might lead to fracture of the particles. However, no such type of fracture of monodispersed, submicron sized (approximately 500 to approximately 600 nm), spherical ZrO_2 particles has been observed, which supports the stabilization of tetragonal phase in the large sized particles.

5   Second, there is substantial evidence (obtained via HRTEM) of little or no free volume in the monodispersed, submicron sized (approximately 500 to approximately 600 nm), spherical ZrO_2 particles. Analogous to the glass transition in polymers, if there were free volume in these large particles, this excess free volume would permit the phase transition to take place. Finally, considering the precursors involved during the sol gel synthesis of

10   ZrO_2 particles, there is no evidence of any group III impurity that might be otherwise stabilizing the tetragonal phase.

Nanosized (approximately 20 to approximately 25 nm) and submicron sized (approximately 500 to approximately 600 nm), monodispersed, spherical ZrO_2 particles are successfully synthesized using the sol-gel technique. The tendency of ZrO_2

15   nanocrystallites (approximately 45 nm) to form hard-aggregates is observed to be responsible for the high-temperature metastable tetragonal phase stabilization, at room temperature, within the submicron sized ZrO_2 particles.

While the invention has been described, disclosed, illustrated and shown in various terms of certain embodiments or modifications which it has presumed in practice,

20   the scope of the invention is not intended to be, nor should it be deemed to be, limited thereby and such other modifications or embodiments as may be suggested by the teachings herein are particularly reserved especially as they fall within the breadth and scope of the claims here appended.